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PREPARATION OF PYROCHLORE FREE PMN-PT POWDER BY WET-CHEMICAL ROUTE

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ABSTRACT

Pyrochlore free Lead Magnesium Niobate-Lead Titanate (PMN-PT) powders with Morphotropic Phase Boundary (MPB) composition were prepared via an intermediate coulombite phase. Coulombite phase was prepared by calcining powder mixtures of magnesium oxalate and niobium oxide processed by wet- chemical method. The powders were calcined in the temperature range of 900-1050°C for 2-5 hours. The complete phase formation is confirmed by XRD analysis. This powder was then properly mixed with lead oxalate and titanium dioxide powder and again calcined in the temperature range of 700-850°C for 2-4 hours to obtain PMN-PT powders. This powder was used to prepare compacts by uni-axial pressing and the compacts were sintered in the temperature range of 1100-1250°C for 2 hours. The compacts were characterized for phase analysis, piezo-properties, morphology etc. The composition was varied to obtain high piezo properties.

INTRODUCTION

Ceramics in the PMN-PT system have important piezoelectric and electrostrictive properties [1-4]. It is a crystalline solid solution between two perovskites. (i) $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) a relaxor ferroelectric with a diffuse phase transition and a broad maximum at ~15°C, and (ii) $PbTiO_3$ (PT), a normal ferroelectric with a sharp phase transition and a curie point (Tc) at 490°C. A morphotropic phase boundary composition has been reported at 35 mole % of $PbTiO_3$, between pseudo cubic and tetragonal phase which has very high piezoelectric properties [5].

The preparation of PMN based ceramics in the perovskite structure requires attention to crystalline phase development. Processing is complicated by the formation of a non ferroelectric pyrochlore phase. The pyrochlore phase is detrimental to the dielectric properties of PMN, because it usually co exists with a lead oxide rich grain boundary phase having low dielectric constant [6]. Pyrochlore phase is invariably in the conventional "mixed oxide" route, however, the amount of pyrochlore can be minimized by using powders of narrow particle-size distribution with high specific surface area and by homogenization [6-7]. However, it is difficult to achieve phase pure perovskite PMN from stoichiometric oxide mixtures due to PbO volatization during calcination. To compensate the loss, PbO up to 6 wt.% excess is added to eliminate pyrochlore phase. The addition of excess MgO (at least 5 mol%) also helps to eliminate the pyrochlore phase[1]. Moreover, the coulombite route proposed by Swartz and Shrout by pre-reacting MgO and Nb_2O_5 before addition of PbO leads to a very low pyrochlore content [5]. The purpose of the present investigation is to prepare pyrochlore free PMN-PT powders at morphotropic phase boundary (MPB) composition. This composition has a very good piezoelectric properties with very high dielectric constant and simultaneously it can be used for both piezoelectric and electrostrictive applications. We have followed the wet chemical method for the preparation of pyrochlore free PMN-PT powder to achieve better properties. It is also known that deficiency of MgO in coulombite stage produces pyrochlore phase after subsequent formation. Therefore, 3% excess MgO powder was used to make sure the product is pyrochlore free.

EXPERIMENTAL PROCEDURE

In wet chemical method the raw materials used were reagent grade basic $MgCO_3$ (Nice chemicals, 99%), fine particle sized Nb_2O_5 powder (SD fine chemicals, 99.5%), Lead nitrate (Loba chemicals,99%), and TiO_2 powder (SD fine chemicals, 99.5%). Required amount of basic $MgCO_3$ was slowly dissolved in 10% oxalic acid solution at room temperature. Nb_2O_5 powder was then dispersed in the above solution with continuous stirring for complete homogenization. The solution was then heated with stirring. In this process magnesium oxalate gets precipitated on fine particles of dispersed Nb_2O_5 powder. The whole solution was then dried up slowly and calcined at 1050°C for 4-6 hours. In the second stage required amount of $Pb(NO_3)_2$ solution was taken and fine TiO_2 powder was dispersed in it and was magnetically stirred. 10% oxalic acid solution was then slowly added to precipitate lead oxalate on TiO_2 surface. pH of the solution was maintained in the range of 2.5-3. The precipitate was then washed and processed to get fine dry powder. Finally this powder was thoroughly mixed with coulombite powder and calcined at 800-850°C for 2-4hours for complete perovskite phase formation. The process flow sheet for preparation of PMN-PT powders is presented in fig.1.The powder was granulated,compacted and sintered at 1150°C/2hr.

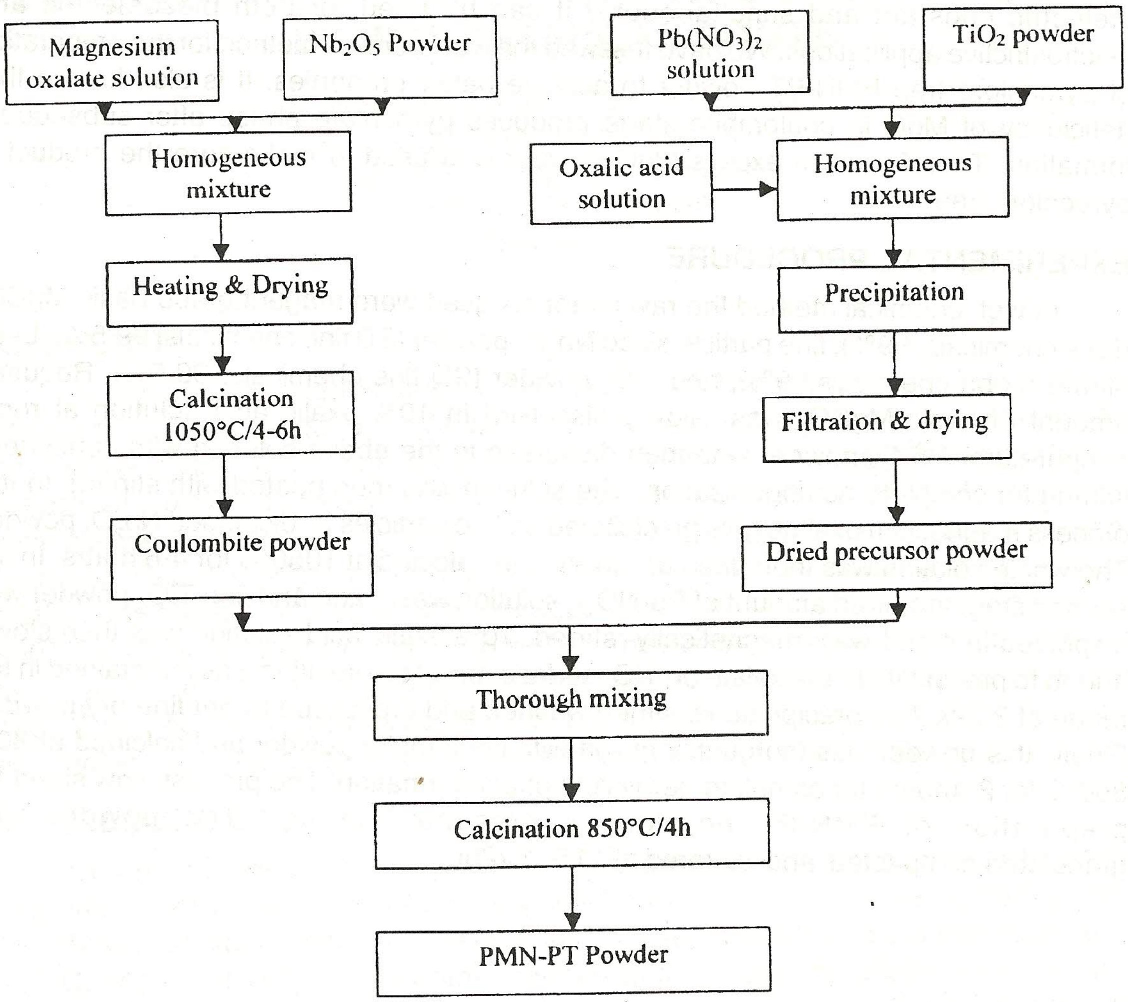

Fig.1: Typical process flow sheet used for preparation of PMN-PT powder

RESULTS AND DISCUSSION:

(1) XRD Analysis

X-ray diffraction analysis was carried out for both coulombite as well as for PMN-PT powders after calcination using CuKa radiation (Figure-2a & 2b). XRD of coulombite powder indicates the complete coulombite phase formation. The X-Ray analysis of the calcined PMN-PT powder reveals a single phase cubic perovskite pattern that essentially corresponded to the PMN-PT solid solutions.

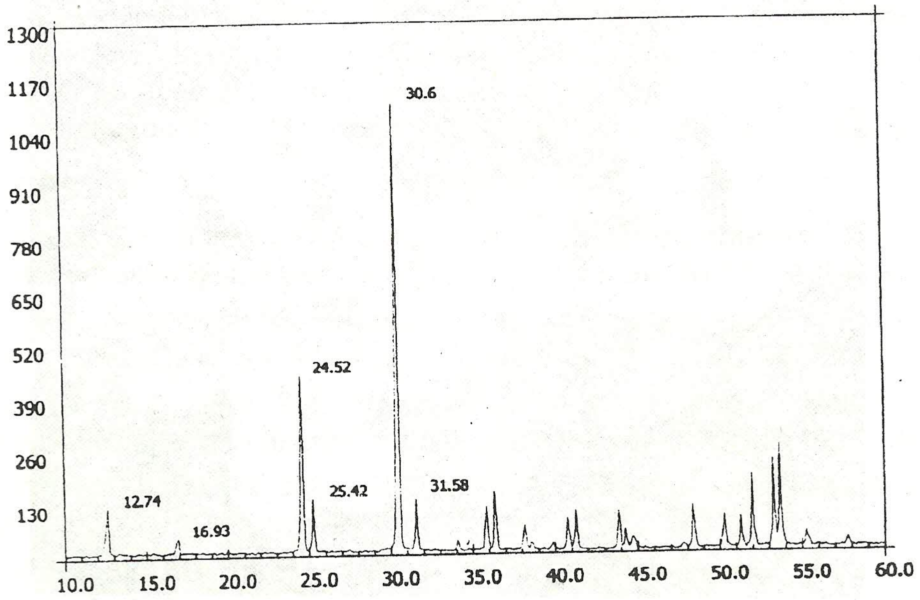

Fig.2a: Typical XRD pattern of Coulombite Powder

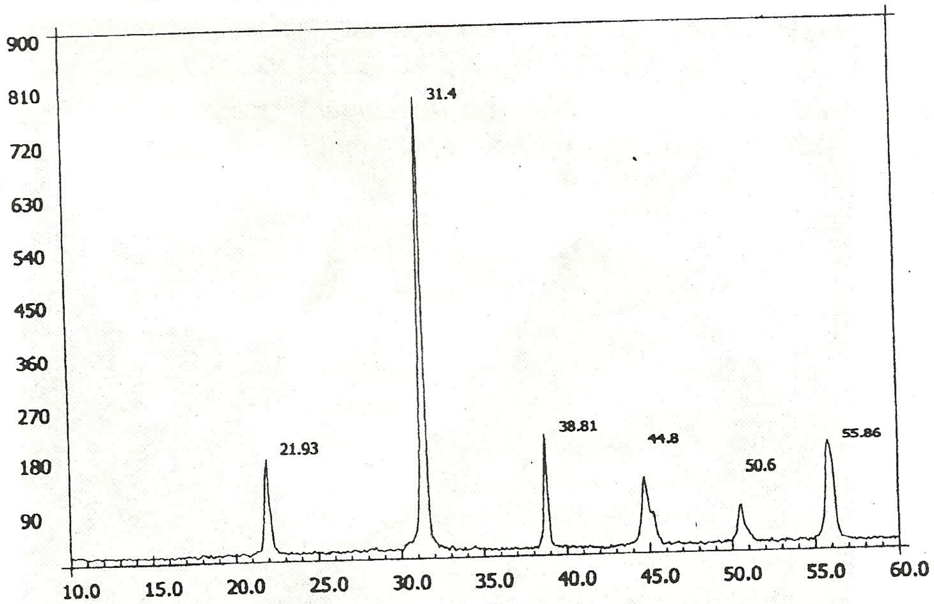

Fig.2b: Typical XRD pattern of PMN-PT Powder

(2) SEM ANALYSIS:

The morphological features of coulombite and PMN-PT powders have been depicted in the SEM pictures in figure 3a and figure 3b respectively. The sub-micron sized coulombite powder and the PMN-PT powder with narrow size distribution are clear from the micrographs. The fineness of these particles contributes for greater reactivity in solid solution reactions.

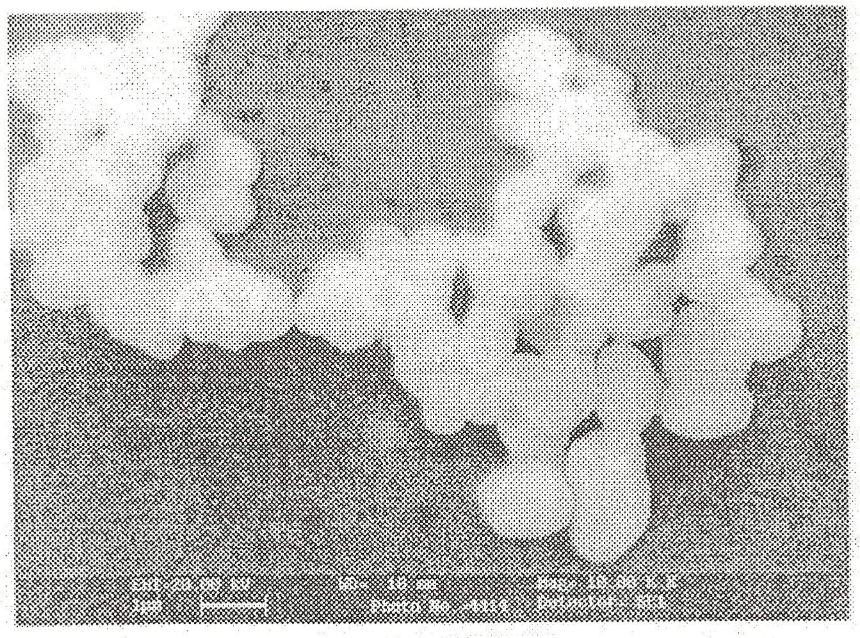

Fig. 3a: Typical SEM micrograph of coulombite powder

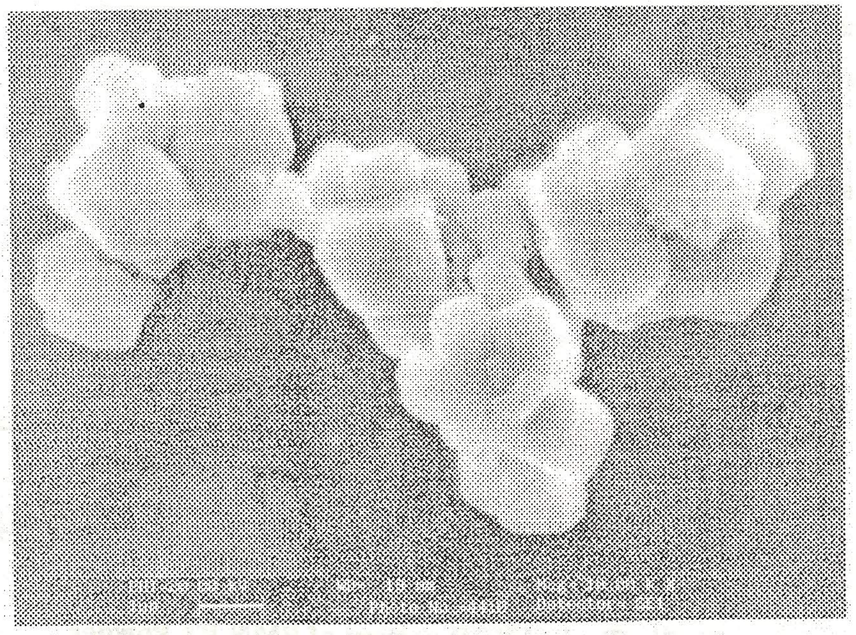

Fig. 3b: Typical SEM micrograph of PMN-PT powder

CONCLUSION:

A high purity PMN-PT perovskite phase was synthesized by the wet chemical route via coulombite route. ors synthesized from a mixture of magnesium oxalate solution and Nb_2O_5. The further processing of powders is going on for sintering studies at different temperature and characterization of piezoelectric and other electrical properties.

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